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Abstract

The methodology for use of a flowing afterglow–Langmuir probe apparatus to measure thermal electron detachment rate coefficients is described. We determined the thermal detachment rate coefficient ($1010 \pm 300\,s^{-1}$) for cyclo-$C_4F_8^-$ ions and the rate coefficient ($1.6 \pm 0.5 \times 10^{-x}\,cm^3\,s^{-1}$) for electron attachment of cyclo-C_4F_8 at 375 K. The sole ionic product of attachment is cyclo-$C_4F_8^-$. The equilibrium constant for the attachment/detachment reaction yields a free energy for attachment at 375 K of $-0.63 \pm 0.02\,eV$, from which we estimate the electron affinity (0 K value) of cyclo-C_4F_8 to be about 0.63 eV.

Keywords: Electron attachment; Electron detachment; Negative ions; Electron affinity

1. Introduction

The flowing afterglow–Langmuir probe (FALP) technique has been used to determine rate coefficients and ionic products for electron attachment for a long list of molecules, including measurements for species which are solid (low volatility) at room temperature (C_{60}) [1] and the only measurements for radicals (CCl_3 and CCl_2Br) [2]. There have been several

review articles on the technique [3,4], and a recent one summarizes the past measurements and describes new work in which both the gas temperature and electron temperature may be varied [5].

Chen et al. [6] and Knighton et al. [7] have pointed out a problem with thermal-energy electron attachment experiments on C_6F_6 that had been carried out using the FALP and drift tube techniques. FALP [8] and drift tube [9] experiments on electron attachment to C_6F_6 showed a dramatic and unprecedented decrease in the apparent attachment rate coefficient above a temperature of 300–400 K. Chen et al. [6] correctly attributed this apparent decrease to thermal electron detach-

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ment from $C_6F_6^-$. At the time, the electron affinity of C_6F_6 was thought to be in the neighborhood of 1 eV, but has since been shown to be 0.52 ± 0.10 eV [10]. Knighton et al. [7] used high-pressure mass spectrometry with an electron scavenger to measure the unimolecular rate for thermal electron detachment from $C_6F_6^-$ in the temperature range 300–350 K. Recently, the drift tube group has used a new apparatus that allows them to determine both attachment and detachment rate coefficients in C_6F_6 gas buffered with a high pressure of nitrogen as a function of temperature [11]. There is now general agreement that the original reports of a rapidly declining attachment rate coefficient for C_6F_6 with increasing 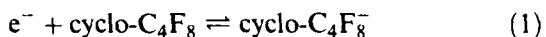temperature came about because the effect of thermal detachment from $C_6F_6^-$ was not recognized. There remains some question as to the effect of buffer gas pressure [11].

The FALP technique has not been previously used to determine thermal electron detachment rate coefficients. We report here results of a study of the effect of thermal detachment from cyclo-$C_4F_8^-$ on electron attachment measurements using a FALP apparatus, and find that under appropriate operating conditions we can determine both the electron attachment and thermal detachment rate coefficients. To this end, it is essential that the attachment reaction is non-dissociative and that the ionic product does not undergo further reaction other than detachment. That is, only the forward and reverse processes in Eqn. (1) are operant:

$$e^- + \text{cyclo-}C_4F_8 \rightleftharpoons \text{cyclo-}C_4F_8^- \qquad (1)$$

The attachment reaction is presumed to create an excited intermediate that is thermalized by the helium carrier gas in a FALP experiment (typically about 130 Pa pressure). The lifetime of the excited $C_4F_8^-$ formed in attachment is $(1.0-1.2) \times 10^{-5}$ s [12,13]; during this time the ions make about 150 collisions with the helium

buffer gas. The Maxwell–Boltzmann distribution of internal energy among the cyclo-$C_4F_8^-$ ions in the carrier gas has a high-energy tail which allows some of the ions to undergo autodetachment. The electron binding energy for cyclo-$C_4F_8^-$ is not known but may be estimated as 0.63 eV from the results of the present work.

Much of the previous work on cyclo-C_4F_8 [12,15–18] has been motivated by the use of perfluorocarbon compounds as dielectrics in electrical devices. The present work on electron attachment to cyclo-C_4F_8 was undertaken as part of a project to determine what effect electron attachment and ion/molecule reactions have on the lifetimes of neutral perfluorocarbon compounds in the earth's atmosphere. Modeling of loss processes for some of these "greenhouse" gases show calculated lifetimes of millennia [19]; the initial modeling indicated that photolysis is the dominant atmospheric loss process for cyclo-C_4F_8. Removal of molecules by electron or ion interactions leads to a significant reduction in the calculated atmospheric lifetime [20]. For cyclo-C_4F_8, the effect of electron attachment on atmospheric lifetime will depend on the fate of the cyclo-$C_4F_8^-$ anion after it has formed. The electron detachment process observed for cyclo-$C_4F_8^-$ in the present work should not affect these lifetimes because the measured detachment rate coefficients are important only for temperatures greater than found in the mesosphere and lower thermosphere.

2. Experimental

The FALP apparatus at Phillips Laboratory is essentially a copy of the FALP apparatus now at the University of Innsbruck [5] and uses data acquisition hardware and software developed at Innsbruck in the past two years. Briefly, the FALP method utilizes a microwave discharge to create an electron/positive-ion

plasma in fast-flowing helium gas (260 atm $cm^3 s^{-1}$, 133 Pa or 1 Torr) in a flow tube of radius 3.64 cm and length 1 m. Between 1–2 Pa partial pressure of argon gas is established downstream of the discharge to eliminate metastable-state helium via Penning ionization. In the present work, octafluoro-cylcobutane (Freon C318) was added to the flowing plasma through an inlet that consists of six hollow needles projecting radially into the flow tube at an axial position 55 cm downstream of the discharge and 45 cm upstream from the mass spectrometer sampling aperture. Because the required flow rate of reactant vapor is small, a 0.64% mixture of cyclo-C_4F_8 in helium was used so that the reactant flow meter could be used on an accurate scale. (The data at 464 K were obtained with neat cyclo-C_4F_8.) The cyclo-C_4F_8 gas was purchased from PCR, Inc., and has an analyzed purity of 99.8%. The helium gas used in the reactant mixtures and as the carrier gas in the flow tube was passed through three liquid-nitrogen cooled molecular sieve traps to remove condensible impurities prior to use. The attachment mass spectra showed only $m/z = 200$ u ion product. We assume the ion observed is cyclo-$C_4F_8^-$. The cyclo isomer of $C_4F_8^-$ has been specifically identified in EPR studies [14] of irradiated cyclo-C_4F_8.

The electron densities along the axis of the flow tube were determined using a movable Langmuir probe, as described in Refs. [3–5]. The Langmuir probe current–voltage characteristic also gives the electron temperature (equal to the gas temperature in a helium buffer) [5]. With no attaching gas present in the flow tube, the decay in electron density along the flow tube axis gives the ambipolar diffusion decay constant ν_D. When the attaching gas is present, measurement of the electron densities allows the electron attachment decay constant ν_a to be determined by fitting the data to the solution of the rate equations describing the

coupled effects of diffusion and attachment [3–5]. In the present work on cyclo-C_4F_8 it was found that the rate equations must be modified to include the effect of thermal detachment in order to fit the data:

$$V_p(\delta n_-/\delta z) = k_a n_r n_e - k_d n_-$$ (2)

$$V_p(\delta n_-/\delta z) = -\nu_D n.$$ (3)

$$\delta n_e/\delta z = (\delta n_-/\delta z) - (\delta n_-/\delta z)$$ (4)

where n_-, n_-, and n_e are the negative ion, positive ion, and electron number densities respectively, and n_r is the concentration of reactant (cyclo-C_4F_8) gas. The electron attachment rate coefficient k_a is equal to ν_a/n_r, and k_d is the thermal detachment rate coefficient. The axial distance downstream of the reactant inlet is z. The plasma velocity, V_p ($\approx 10^4 cm s^{-1}$), was measured by pulse-modulating the plasma density and timing the arrival of the disturbance (a few percent drop in n_e) at the Langmuir probe at six axial positions over a distance of 20 cm in the reaction zone. The cyclo-C_4F_8 number density was set at least 18 times the initial ($z = 0$) electron density so that an assumption of pseudo-first-order kinetics in the attachment is justified.

The two basic assumptions involved in the use of Eqns. (2)–(4) have been discussed in Ref. [1]: (a) the loss of positive ions is by diffusion only, and (b) the negative ions are lost only by thermal detachment. Assumption (a) is easily justified in our situation when n_r is as small as $7 \times 10^{11} cm^{-3}$ and $n_e < 4 \times 10^9 cm^{-3}$ because few molecular ions will be produced in the reaction zone, and electron–ion or ion–ion recombination loss of positive ions is negligible in any case with low plasma density. Assumption (b) is satisfied because the diffusive loss of negative charge from the plasma may be attributed to the highly mobile electrons even when n_- exceeds n_e by a factor of 10–100 [21,22]. Biondi [21] and Oskam [22]

used expressions for particle current densities (which have a diffusive term and a mobility term) for electrons, negative ions, and positive ions in the plasma, and found that the neutrality condition (analogous to Eqn. (4)) required the ambipolar diffusion coefficients $D_{a,+}$, $D_{a,e}$, $D_{a,-}$, for the three species to be

$$D_{a,+} \approx 2D_+ \tag{5}$$

$$D_{a,e} \approx 2D_-(1 + n_-/n_e) \tag{6}$$

$$D_{a,-} \approx 2D_+(1 + n_-/n_e)(D_-/D_e) \tag{7}$$

where D_+, D_-, and D_e are the free diffusion coefficients (proportional to the respective mobilities) of the three charged species in the plasma. Note that in the absence of negative ions there is only one ambipolar diffusion coefficient, $D_a = 2D_+$. Negative ions diffuse against the space-charge field of the plasma, and indeed Eqn. (7) shows $D_{a,-}$ to be negligible since the mobility of an electron is typically 1000 times that of a negative ion [21] (and thus $D_-/D_e \approx 0.001$ for our situation where the electron temperature is the same as the gas temperature). Because of this, as the density of negative ions grows, the probability that a particular electron will be lost to diffusion increases proportionately, i.e., $D_{a,e}$ increases with n_-/n_e in order to balance the diffusive wall current of positive ions. We reiterate that Eqns. (5)–(7) are certainly valid as long as n_- is no more than 10 times n_e; at some point, the space-charge field collapses and the plasma becomes a negative-ion/positive-ion plasma with a different diffusion coefficient [22]. These points regarding diffusion are emphasized here because the results below — both experimentally and in solutions of Eqns. (2)–(4) — show that for a steady-state diffusing plasma of constant n_-/n_e the decay rates of the electron and positive ion densities are both described by the diffusion decay constant ν_D measured in the absence of negative ions (in the absence of attaching gas). The diffusion decay constant

ν_D is equal to the ambipolar diffusion coefficient divided by the square of the diffusion length characteristic of the apparatus [2].

3. Determination of k_a and k_d

The analytic solution to Eqn. (3) (exponential diffusive decay) was used at incremental z values, while Eqns. (2), (4) were solved numerically for n_e as a function of z, analogous to the method used in Ref. [2] for a different problem (electron attachment to radicals). The numerical solutions were checked in various limiting cases where the solutions are known. We repeat that ν_D was determined separately in the absence of reactant gas. The electron density at $z = 0$ cannot be measured directly because the reactant inlet port disturbs the plasma flow in the neighborhood of the port. The effective electron density at $z = 0$ is obtained by extrapolating the diffusion-only data to $z = 0$. In finding the best fit to the attachment/detachment data, n_e ($z = 0$) may be adjusted slightly, accounting in effect for drift in n_e ($z = 0$) which may have occurred between the diffusion-only and the attachment/detachment data runs. Such an adjustment moves the calculated curve in Fig. 1 up or down without changing its shape. Fig. 1 shows a fit of the solution for n_e to data obtained in a helium buffer at 375 K. A starting value of k_a, 9×10^{-9} cm^3 s^{-1}, was obtained using our usual data analysis procedure (i.e., without considering thermal detachment), by fitting only the first few points (low z) shown in Fig. 1, where thermal detachment should have less impact since there are more electrons than cyclo-$C_4F_8^-$ at low z. The calculated curves in Fig. 1 show that this approximation is reasonably valid only for the first two centimetres or so following the reactant inlet port. Not surprisingly, a larger value of k_a, 1.65×10^{-8} cm^3 s^{-1}, is needed to fit the entire range of the data, along with a k_d value of
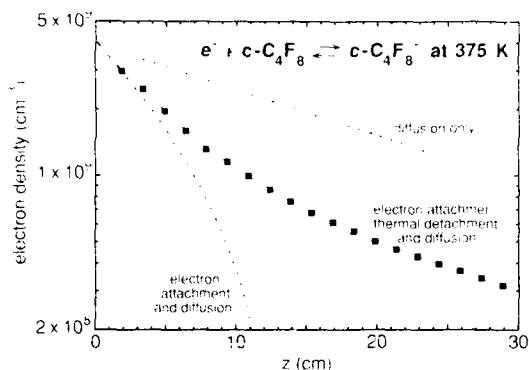
Fig. 1. Electron density along the axis of the flow tube showing approach to steady-state diffusive loss at large z, for the electron attachment detachment reaction with cyclo-C_4F_8 (7.34× 10^{10} cm^{-3}) at 375 K, in a helium carrier gas (2.59 × 10^{16} cm^{-3}). The plasma velocity was 10020 cm s^{-1}; (— — —) and (· · — · ·): solutions to Eqns. (2)–(4) for the conditions indicated.
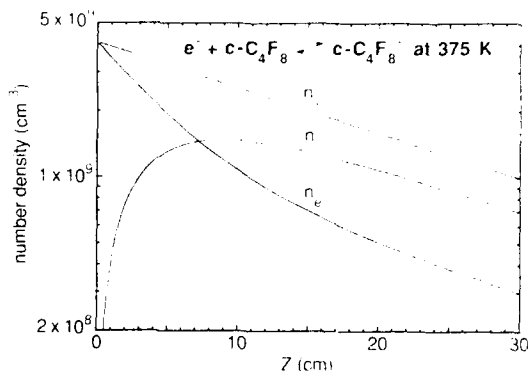

Fig. 2. Calculated electron, negative ion, and positive ion densities along the axis of the flow tube, for the diffusion, attachment, and detachment parameters derived from the data shown in Fig. 1, indicating the approach to steady state by each of the charged species in the plasma.

986 s^{-1}. Fig. 1 also indicates the behavior that would be expected if the thermal detachment process were not active ($k_a = 1.65 \times 10^{-8}$ cm^3 s^{-1} and $k_d = 0$). The data shown in Fig. 1 are ideal for obtaining k_a and k_d, because the values $\nu_a = 1211$ s^{-1} and $k_d = 986$ s^{-1} are comparable in magnitude, and both are adequately larger than ν_D (475 s^{-1}) so that diffusion errors in the determination of k_a (= ν_a/n_r) and k_d are lessened. Three other data sets were obtained at 375 K, one in which the initial electron density was 50% lower than in Fig. 1, and two in which the cyclo-C_4F_8 concentrations were lower than in Fig. 1. Average values from the four data sets at 375 K are $k_a = 1.6 \pm 0.5 \times 10^{-8}$ cm^3 s^{-1} and $k_d = 1010 \pm 300$ s^{-1}.

It is instructive to plot n_e, n_+, and n_- for the attachment/detachment approach to steady state, using the rates obtained from the 375 K data. Figure 2 shows that (a) at all times the positive ion diffusion rate is the same as that measured in the pure electron–ion plasma; (b) the electron density falls at a faster rate initially because of the additional loss to attachment, but in steady state has the same diffusion rate as the positive ions, and (c)

although the negative ions have negligible diffusive loss, the attachment/detachment interchange results in n_- showing the same decay with time (or distance along the flow tube) because of diffusive loss during the free-electron phase.

Data were also obtained at 464 K. The detachment reaction was so strong (≈ 3400 s^{-1}) that an unusually large amount of reactant gas was needed (10^{13} cm^{-3}) in order to achieve significant decrease in the electron density from attachment. As a consequence of the high reactant concentration, the electron density decrease took place within a few centimetres of the reactant inlet port and was difficult to fit to the rate expressions with any confidence. Also, a large concentration of cyclo-C_4F_8 resulted in a lowering of ν_D because ion/molecule reactions change the positive-charge carrier from He$^+$ and Ar$^+$ to $C_xF_y^+$ ions, and this lowering of the asymptotic slope observed in n_e vs. z at large z had to be accounted for in the modeling, further complicating the data-fitting process. (An effective ion/molecule reaction rate coefficient of 7.2 × 10^{-11} cm^3 s^{-1} was needed to account for the change in diffusion decay constant, and values of $k_a = 1 \times 10^{-9}$ cm^3 s^{-1} and $k_d = 3400$ s^{-1} were obtained

in the fit shown in Fig. 3.) The 464 K data and fitted curves are shown in Fig. 3 for the purpose of illustrating a limitation of the method. The modeling calculations imply that a better choice for n_r at 464 K would have been a value for which $\nu_a \approx k_d$. A slower approach to steady state might have allowed more accurate determination of k_d and k_a but would still be limited by the change occurring in ν_D.

Once the results at 375 and 464 K were obtained, showing quite obviously effects of thermal detachment, data acquired at 303 K were re-examined. These data are shown in Fig. 4; the decay in electron density covers an order of magnitude. Our original analysis of these data (not considering thermal detachment) did not indicate significant (or systematic) deviation from the simple attachment case customarily employed to fit the FALP data. A fit with our usual analysis protocol (i.e., $k_d = 0$) was not perfect, but satisfactory — the lowest one or two points fell above the best-fit attachment/diffusion curve, but not alarmingly so, as the experimental uncertainty in the low-n_e points is greater than for large n_e. The fit gave $k_a = 1.1 \times 10^{-8}\,\mathrm{cm^3\,s^{-1}}$. Re-analysis using numerical solutions to Eqns. (2)–(4) showed that thermal detachment has a more significant effect than is first apparent. The revised fits to the two data sets available at 303 K (for two cyclo-C_4F_8 concentrations differing by a factor of two) both yielded $k_a = 1.5 \pm 0.5 \times 10^{-8}\,\mathrm{cm^3\,s^{-1}}$ and an average value of $k_d = 260 \pm 260\,\mathrm{cm^3\,s^{-1}}$. The large uncertainty in k_d is a consequence of the relatively small thermal detachment rate coefficient ($260\,\mathrm{s^{-1}}$) for the fit shown in Fig. 4, compared with the attachment ($960\,\mathrm{s^{-1}}$) and diffusion $347\,\mathrm{s^{-1}}$) decay constants, and the few data points that had been obtained at 303 K.

4. Determination of equilibrium constant
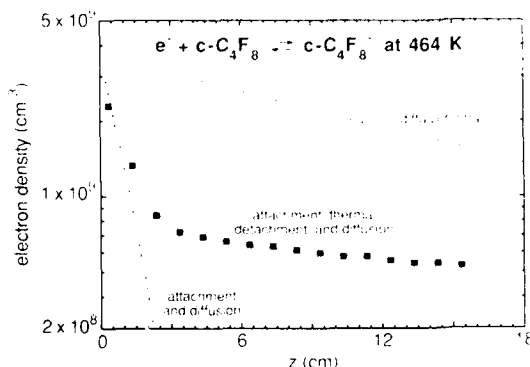
The equilibrium constant for the attach-

Fig. 3. Electron density along the axis of the flow tube for the electron attachment detachment reaction with cyclo-C_4F_8 (10^{13} cm³) at 464 K, in a helium carrier gas (2×10^{16} cm³) The plasma velocity was 10600 cm s⁻¹; (—) and ( ) solutions to Eqns. (2) (4) for the conditions indicated.

ment/detachment reaction (1) is given by [23]:

$$K_a = k_a/k_d \tag{8}$$

In Fig. 1 it appears that reaction (1) essentially reaches steady-state diffusive loss at distances beyond 28 cm from the reactant inlet port, because the slope of the attachment detachment curve is the same as that of the diffusion-only line, within the small scatter in the data.

Under conditions in which equilibrium is established, $\delta n_-/\delta z$ in Eq. (2) is zero at large z, resulting in an alternative expression for K_a [24]:

$$K_a = [n_-/n_e n_r]_{eq} \qquad \text{Equilibrium case} \tag{9}$$

This expression is not applicable with the FALP experiments because equilibrium is never attained. The rate equations (2)–(4) show that all of n_+, n_-, and n_e follow (ambipolar) diffusion-limited decay slopes at large z, as illustrated in Fig. 2. That is, $\delta n_-/\delta z$ may become constant at large z, but not zero because of diffusive loss. Thus, in the case of the FALP experiments, steady state in the decay slopes occurs at large z if:
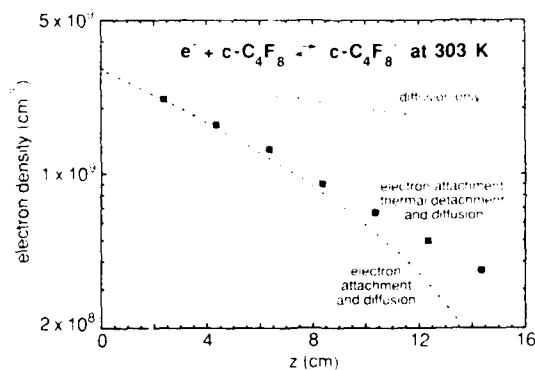
$$V_p(\delta n_-/\delta z)_{ss} = -\nu_D n_- \tag{10}$$

Fig. 4. Electron density along the axis of the flow tube for the electron attachment detachment reaction with cyclo-C$_4$F$_8$ (6.40 × 10^{10} cm^{-1}) at 303 K, in a helium carrier gas (3.22 × 10^{16} cm^{-1}). The plasma velocity was 9905 cm s^{-1}; ( ) and (-): solutions to Eqns. (2) (4) for the conditions indicated.

which leads to

$$[n_-/(n_e n_r)]_{SS} = k_a/(k_d - \nu_D) \tag{11}$$

Therefore, values of n_- and n_e at steady state (large z) cannot be used to calculate K_a as is done in equilibrium experiments (Eqn. (9)): a diffusion correction is required in FALP experiments:

$$K_a = [n_-/(n_e n_r)]_{SS}[1 - (\nu_D/k_d)]$$

steady-state case $\tag{12}$

For pseudo first-order kinetics to hold, we set $n_r \gg n_e$; that is, n_r is effectively constant, and therefore n_-/n_e is also constant at large z, as is evident in Fig. 2. Since the magnitude of the $[1 - (\nu_D/k_d)]$ correction can only be determined by first fitting the data to obtain k_d (and k_a), from which K_a may be calculated directly, Eqn. (12) does not give an independent method of determining K_a and therefore has limited usefulness for FALP experiments.

Note that Eqn. (11) implies that the steady-state condition is not always reached in FALP experiments. If $k_d < \nu_D$ the plasma diffuses away before steady state is reached; the data of Fig. 4 provide an example, since k_d (≈ 260 s^{-1}) for those data is less than ν_D

(347 s^{-1}). Note also that Eqn. (10) does not imply that the negative ions contribute to diffusion; the effect at large z is a result of the attachment detachment interchange between n_- and n_e.

The equilibrium constant found from Eqn. (8), using $k_a = 1.6 \times 10^{-8}$ cm^3 s^{-1} and $k_d = 1010$ s^{-1} from the present work, is $K_a = 1.58 \times 10^{-11}$ cm^3 at 375 K.

While the uncertainty in k_a and k_d is $\pm 30\%$, K_a depends only on the relative accuracy. We estimate the uncertainty in K_a to be $\pm 20\%$ based on a sensitivity analysis with the data-fitting procedure, and on the statistical variation observed in different data sets. To give one example, if k_a is fixed at a value 20% lower than the best-fit value for the data of Fig. 1, k_d must be lowered by 8% to achieve a reasonable fit to those data. (This fit, with a low value of k_a, clearly overestimates the electron densities at intermediate values of z, but fits densities at low and high z). Thus, in this example for k_a 20% low, K_a turns out to be 15% low.

5. Determination of the free energy for electron attachment

K_a may be normalized to standard pressure by multiplying by the gas concentration at 1 atm pressure and 375 K, giving $K_p = 3.10 \times 10^8$. Then, the free energy ΔG for the attachment reaction is given by

$$\Delta G = -kT \ln K_p = -0.63 \text{ eV} \tag{13}$$

6. Determination of enthalpy for electron attachment

The entropy change ΔS in the attachment reaction (1) is calculated from

$$\Delta S^\circ = S^\circ(\text{cyclo-C}_4\text{F}_8^-) - S^\circ(\text{cyclo-C}_4\text{F}_8)$$
$$- S^\circ(e^-) \tag{14}$$

Here, the S terms are the constant-pressure entropies of cyclo-C_4F_8, cyclo-$C_4F_8^-$, and the electron, respectively. S (e$^-$) at 375 K is interpolated from values given in the JANAF tables [25] and adjusted for 1 s.t.p. atm reference pressure, or evaluated from

$$S \ (\text{e}^-) = k \ \ln[2(ekT)^{5/2}(2\pi m_e)^{3/2}(p \ h^3)^{-1}]$$

(15)

where k is Boltzmann's constant, h is Planck's constant, e is the base of the natural logarithm, m_e is the electron mass, and p is the reference pressure (1.013 kPa). The leading factor of two inside the brackets of Eqn. (15) is the spin multiplicity of the electron. Since the S terms of Eqn. (14) all have logarithmic dependences, we only need the ratio of the arguments of the logarithm function for cyclo-$C_4F_8^-$ and cyclo-C_4F_8. The major contribution to this ratio is in the electron spin degeneracies, 2 for cyclo-C_4F_8, and 1 for cyclo-$C_4F_8^-$ (the electron in the anion is presumed to be in a non-degenerate orbital [14]). The translational contributions cancel, and the rotational contributions will largely cancel since the symmetry of the anion and neutral is the same. The vibrational partition function may in fact not cancel if there is an appreciable "softening" of the vibrational frequencies upon anion formation; this would lead to a small positive contribution to ΔS [23]. In any case, ΔS affects ΔH only at the 10% level. Thus,

$$\Delta S = k \ \ln 2 - k \ \ln[2(ekT)^{5/2}(2\pi m_e)^{3/2}$$

$$\times (p \ h^3)^{-1}]$$

(16)

$$\Delta S = -2.060 \times 10^{-4} \text{eV K}^{-1}$$

(17)

We can now obtain the enthalpy for the attachment reaction at 375 K

$$\Delta H = \Delta G + T\Delta S = -0.71 \text{eV}$$

(18)

The procedure above may be summarized with the formula

$$K_a = 1.700 \times 10^{-17} \text{cm}^3 \langle g_A \ g_{A^-} \rangle T^{3/2}$$

$$\times \exp(-\Delta H / kT)$$

(19)

where g_A and g_{A^-} are the degeneracies of the neutral and negative ion, respectively.

The $\pm 20\%$ uncertainty in K_a affects ΔH by 1% since ΔH depends only logarithmically on K_a. Even if the absolute uncertainties in k_a and k_d (30%) are combined to give a maximum 60% uncertainty in K_a, ΔH is only affected by a few percent. Hence, the attachment detachment equilibrium technique should yield accurate ΔH. Additional confidence in ΔH deduced in this manner may be gained from experiments in which the carrier gas pressure is varied, to ensure thermalization of the negative ions formed in the attachment process, and from measurements at other temperatures. (The present result is based only on data at 375 K, because the 303 K and 464 K data are not considered reliable. Nevertheless, the 303 and 464 K data yield values for the electron affinity of cyclo-C_4F_8 that are within 0.08 eV of that obtained from the 375 K data, below.) We plan to undertake more complete experiments in the near future, for several molecules.

7. Estimate of the electron affinity of cyclo-C_4F_8

The electron affinity (EA, defined at 0 K) of cyclo-C_4F_8 is related to the value of ΔH found at 375 K by

$$EA = -\Delta H_{375} + \int_0^{375} C_p(A^-) dT$$

$$- \int_0^{375} C_p(A) dT - \int_0^{375} C_p(\text{e}^-) dT$$

(20)

where C_p are temperature-dependent specific

heat functions for A = cyclo-C_4F_8, A = cyclo-C_4F_8, and for the electron. The specific-heat function is not known for cyclo-C_4F_8. If we assume that the integrated specific heat is approximately the same for both cyclo-C_4F_8 and cyclo-C_4F_8, then only that for the electron need be evaluated. We obtain

$$\int_0^{375} C_p(e^-)\, dT = \tfrac{5}{2}kT = 0.081\,\text{eV} \qquad (21)$$

as given in the JANAF tables [25]. Eqn. (20) then yields an estimate of the electron affinity of cyclo-C_4F_8 of 0.63 eV.

8. Previous work

Thermal electron detachment was first observed for O_2^- [26] using a drift tube apparatus. Thermal detachment has since been observed for a large number of negative ions using the electron capture detector (ECD) method (see Ref. [6] and [27]), starting with aromatic hydrocarbon anions [28]. Measurements of thermal detachment rate coefficients are few, however, and include those for O_2^- [26], NO^- [29–31], azulene anions [32,33], $C_6F_6^-$ [7,11], and $C_4F_6^-$ [34]. For O_2^- [26] and NO^- [30], drift tube measurements of both the (ternary) electron attachment and (binary) thermal detachment rate coefficients in the same experiment enabled the accurate calculation of the electron affinities of O_2 and NO, respectively. The ECD method makes use of the detachment process to determine electron affinities [27]. In other cases [7,29,32], results on thermal detachment have been shown to be consistent with accepted electron affinities. Excellent discussions of the process and measurements of detachment rates have been given by Knighton et al. [7], Grimsrud et al. [32], and Kebarle and Chowdhury [23].

The electron attachment rate coefficient determined here for 303 K, $k_a = 1.5 \pm 0.5 \times 10^{-8}\,\text{cm}^3\,\text{s}^{-1}$, may be compared with previous results (in units of $10^{-8}\,\text{cm}^3\,\text{s}^{-1}$) at 298–300 K: 1.25 [15], 1.11 [16], and 1.2 [17]. Although the present k_a agrees with the previous values within experimental uncertainty, it is worth noting again that if thermal detachment was not taken into account the fit to the present data at 303 K yields $k_a = 1.1 \times 10^{-8}\,\text{cm}^3\,\text{s}^{-1}$. It is likely that the previous experimental values suffer similarly. There are no previous measurements of k_a other than at room temperature with which to compare our results. Chutjian and Alajajian have shown that the attachment is due to an electron scattering resonance around zero energy [35].

The maximum s-wave attachment rate coefficient at 300 K is $5 \times 10^{-7}\,\text{cm}^3\,\text{s}^{-1}$ [36]. A more realistic maximum is the electron-capture rate coefficient of Klots [36]. For a cyclo-C_4F_8 polarizability of $1.2 \times 10^{-23}\,\text{cm}^3$ (estimated from the polarizabilities of similar molecules [37]) the Klots formulation gives an electron-capture rate coefficient of $3.4 \times 10^{-7}\,\text{cm}^3\,\text{s}^{-1}$ at 300 K. Thus, the measured rate coefficient corresponds to an electron attachment event in one out of every 23 collisions at room temperature.

9. Conclusions

We have described methodology for using the FALP technique for measuring thermal electron detachment rate coefficients. We have determined both the electron attachment rate coefficient ($k_a = 1.6 \pm 0.5 \times 10^{-8}\,\text{cm}^3\,\text{s}^{-1}$) and the thermal detachment rate coefficient ($k_d = 1010 \pm 300\,\text{s}^{-1}$) for cyclo-$C_4F_8$ at 375 K. The method is shown to be most accurate when the experimental conditions are such that the attachment decay constant ($k_a n_r$) and the detachment rate coefficient (k_d) are similar in magnitude, with both larger than the diffusion decay constant. In other situations, where either k_a or k_d dominates, or where the neutral reactant concentration is large enough that ion–molecule

reactions alter the positive ion identity, the thermal detachment rate cannot be determined accurately. Even when the effect of thermal detachment is not at all obvious (as with cyclo-C_4F_8 at 303 K), thermal detachment can have a significant effect on the value of k_a derived from the data.

The equilibrium constant for the attachment/detachment reaction (1) has been obtained at 375 K, and yields the free energy for the attachment reaction at this temperature, $\Delta G^\circ = -0.63 \pm 0.02$ eV. Assuming the partition functions for cyclo-$C_4F_8^-$ and cyclo-C_4F_8 are equal except for the electron-spin degeneracy, we obtain the enthalpy of the attachment reaction at 375 K, -0.71 eV. Assuming the integrated specific heats for cyclo-$C_4F_8^-$ and cyclo-C_4F_8 are similar, we are able to estimate the electron affinity of cyclo-C_4F_8 as 0.63 eV. A review of previous work on attachment/detachment equilibrium, especially with O_2 [26] and NO [29,30], leads us to believe that perfection of this technique with the FALP apparatus will enable accurate measurements of electron affinities for molecules possessing relatively low electron affinities, perhaps < 1 eV. This method is only applicable if the electron attachment process is non-dissociative, and if the negative ion product of attachment does not react with the parent neutral.

Acknowledgments

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